CHARACTERIZATION OF SOLID FUEL BY POME

Muhammad Najmi Bin Mohd Shah, Ku Halim Ku Hamid,

Faculty of Chemical Engineering, Universiti Teknologi MARA

***Abstract* – The palm oil industry is recognized as one of the major agriculture contributions to the abundant production of oil palm solid wastes. Hence, this study is aimed at investigating the solid fuel characterization of Palm Oil Mill Effluent (POME) using Thermogravimetric analysis (TGA). The heating value (HHV), ultimate and proximate analysis was determined using standard ASTM techniques. Consequently, the thermal decomposition behavior of the fuel was determined by heating the sample from 50°C to 900°C in a thermogravimetric analyzer (TGA) at 10°C per min heating rate. The ultimate and proximate analysis revealed that POME powder contains low moisture content, ash content and high fixed carbon, volatile matter content while the HHV was 17.57 MJ/kg. In addition, TGA results indicated thermal decomposition of the fuel occurs in four stages. Devolatilization commenced at 206°C with a peak devolatilization temperature (Tmax) of 400°C respectively resulting in 80% weight loss. From Fourier Transform Infra-Red Spectroscopic (FTIR), it shows the major functional group in solid POME which was alcohol, hexanoic acids, butyraldehyde, alkenes group, and alkyl halides. As a conclusion, solid POME is suitable to be used as solid fuel because it is environmentally friendly.**

***Keywords*— Derivative Thermogravimetric (DTG), Elemental Analyzer, Fourier Transform Infra-Red spectroscopic (FTIR), High Heating Value (HHV), Palm Oil Mill Effluent (POME), Proximate Analysis, Thermogravimetric Analyzer (TGA), Volatile Matter (VM).**

I. INTRODUCTION

Palm oil production increased dramatically in 2010 due to advanced technology production, good system management and market demand from the palm oil industry. The demand in Malaysia was up to 17 million tons of palm oil and over 2 million tons of palm kernel oil, which made Malaysia becomes the 27% of world's export trade of oils and fats and 12% of world's oil and fat production [1]. The production of abundances biomass wastes was generated mainly by milling and plantation activities [2].

There are some improvements in order to make it more economical and environmentally friendly by introducing a National Biomass Strategy 0202 that focusing on oil palm biomass as a starting point.[3]. Reducing the cost of disposal of unused material is a good strategy in order to gain more profit from biomass wastes. Malaysia already used biomass wastes as an alternative source for generating steam and producing electricity by combusting mesocarp fiber (MF) and palm kernel shell (PKS) [4].

The new renewable energy technology has been developed in order to tackle the energy crisis. These technologies are very useful in order to make it as backup energy since the energy sources from other renewable petroleum-derived limited and cannot sustain for the next 100 years [5].

A wide variety of fuels are used in households in developing countries for cooking and heating. Solid fuels refer to both biomass fuels and coal [6]. The most common fuel used for cooking and heating is wood, followed by other solid biomass fuels, such as charcoal, dung, agricultural residues and sometimes even leaves and grass. These fuels are often collected from the local environment in rural areas and are purchased through markets in urban areas [7].

In some rural areas, farmers who own or manage livestock have the option of using a digester to turn dung and agricultural waste into biogas, which is a fuel that can be used for both heating and lighting [8]. Electricity is not commonly used in developing countries for cooking but is often used for other purposes, such as lighting and powering appliances[4]. In China and some coal-producing regions in India and South Africa, coal is used as a cooking and heating fuel, sometimes in combination with other biomass fuels. Raw coal may be used in many forms from lumps to briquettes to fine powders [9]. Coal may be processed as simply as forming coal balls or cakes by hand followed by sun-drying or may undergo a sophisticated procedure, such as being blended into a uniform mixture with binders to reduce sulfur and particulate emissions and formed into briquettes designed to burn efficiently and cleanly in special stoves [2].

Palm oil mill effluent (POME) known as abundant biomass waste that being produce by plantation and milling due to high demand for oil palm production [10]. Therefore, for better economic and environmental values POME had been used as alternative energy replacement in Malaysia [5]. Unfortunately, one of the main issues for using POME is their availability to act as solid fuel. Moreover, the properties of oil palm biomass waste are low calorific value, high moisture content, hygroscopic nature, and high oxygen content make it have limited biomass usage as fuel [11].

Therefore, this research conducted to characterize solid fuel production from palm oil mill effluent (POME). There are several analyses will be conducted to determine the effectiveness of POME as solid fuel such as proximate analysis, ultimate analysis, calorific value, elemental analysis, IR spectrum analysis, and TGA.

II. METHODOLOGY

A. Palm Oil Mill Effluent (POME)

The POME used in this study was acquired from Sime Darby Plantation Berhad, Pulau Carey, Selangor, Malaysia. 10L of POME was supplied. POME also contains substantial quantities of solids; both suspended solids and total dissolved solids in the range of 18,000 and 40,500 mg/L, respectively. This wastewater was collected from the production of crude palm oil.

B. Preparation of POME powder

The liquid POME was poured into 50mL beaker before drying and measured weight. The POME solution was dried using a

microwave oven until became powder. The duration for drying was 30 min at range 80℃ to 120℃. After dried the weight of solid POME was being measured and the percentage by mass was calculated. *Caution: Always aware with the time taken for the drying process to make sure POME dried completely.*

C. Elemental Analyzer

Carbon, hydrogen, nitrogen, and sulfur (CHNS) are fundamental elemental components that are analyzed by using Thermo Electron Corporation FlashEA 1112 CHNS elemental analyzer. Proximate analysis was carried out according to ASTM standard techniques for determining the moisture content, volatile matter, ash content and fixed carbon content of biomass fuels [12].

D. Fourier Transform Infra-Red spectroscopic (FTIR)

The solution was weight to measure the percentage of the solid powder obtained. The resulting solid powder was analyzed on ultimate analysis using Spectrum One 74630 analyzer. The higher heating value (HHV) of the POME solid powder was determined using a bomb calorimeter (IKA calorimeter system, Model C2000). A Fourier Transform Infra-Red spectroscopic (FTIR) analyzer (Model Perkin Elmer Spectrum One) with a scan resolution of 0.5 cm^{-1} to 64 cm^{-1}, scan range 4000cm^{-1} to 500cm^{-1} and scan number 16, was used to analyze and obtain the IR spectrum of the sample.

E. Thermogravimetric analyzer (TGA)

Consequently, the thermal decomposition behavior of the fuel was determined using a thermogravimetric analyzer (TGA) Model Mettler Toledo TGA/DSC 1. Approximately 20 mg of the solid PONE was placed in an Aluminum sample holder and heated from 50 °C to 900 °C at 10 °C/min heating rate using nitrogen (N_2) (flow rate of 25 ml/min) as the sweeping gas.

F. Bomb calorimeter

Combustion is the chemical combination of a combustible fuel with oxygen in producing heat energy. Combustion is achieved by combining the two key elements of combustion fuel and energy. This basic functionality required for such solid or liquid fuel to act as the initiator of the combustion process. Most fuels contain carbon or carbon and hydrogen where involving the oxidation of carbon to carbon dioxide and water as waste products. A good fuel should have high calorific value and in doing so should produce large quantities of heat energy when combusted.

III. RESULTS AND DISCUSSION

A. Fuel Characterization

The ultimate and proximate analyses of POME solid powder is presented in Tables 1 and 2 respectively.

Table 1: Ultimate analysis of POME solid powder (wt., %)

Element	*POME solid powder*
Carbon	51.78
Oxygen	32.54
Hydrogen	5.20
Nitrogen	5.10
Magnesium	0.82
Aluminum	1.16
Silicon	1.70
Phosphorus	1.20
Sulphur	2.69
Chlorine	0.69
Potassium	2.82
Calcium	2.29
Iron	2.32

Dried POME contained carbon (C) as the main chemical composition as shown in Table 1 followed by oxygen (O), hydrogen (H), nitrogen (N), sulphur (S), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), aluminum (Al), iron (Fe), silicon (Si) and chlorine (Cl). Considering C, H, O, as the main biomass constituent elements, the empirical formula $CH_{5.2}O_{32.54}$ was determined from the ultimate analysis of the solid POME. The solid POME contained trace amounts of nitrogen and sulfur content indicating the thermal conversion of the fuel will result in low concentrations of SO and NO. It was evidenced that POME does not contain toxic heavy metals (Pb, Cd, Hg, Mn, and Cr), thus handling POME can be considered as environmentally safe.

Table 2: Proximate analysis of POME solid powder (wt., %)

Biomass Component	**POME solid powder**
Moisture Content	8.17
Volatile Matter	71.83
Fixed Carbon	15.44
Ash	4.56
HHV, MJ/kg (dry basis)	17.57
LHV, MJ/kg (dry basis)	16.22

The proximate analysis showed that the POME solid powder contains low moisture content less than 10 %, ash content less than 5 %, and fixed carbon higher than 20 %. The volatile matter content was lower than 70 %. All the result shows there were differences in the value of the biomass compound with the previous studies by Yen Yee Chong et al [13]. However, the fixed carbon content of the powder was significantly greater than the values reported for POME in Table 2. This may be due to the thermal and physicochemical properties of the solid powder.

Fixed carbon is the solid carbon found in POME sludge in previous studies obtained after the devolatilization or pyrolysis of biomass [14]. It is not a static property of biomass fuels since the conversion of volatile matter (VM) in biomass into char is largely dependent on the heating rate [8]. Table 3 shows the differences in calorific value between several samples. All the other samples were taken from the previous studies [15], [16] and [17].

Table 3: Calorific value of the different sample.

Materials	**Calorific value (MJ/kg)**
Palm oil mill effluent	15.90
Empty fruit bunches	17.08
Brown coal	14.30
Complete dry woods	18.50

From the result shows in Table 3 were the differences in calorific value from EFB, brown coal, and complete dry woods. It shows that POME has the lowest value due to high concentration volatile matter. However, it also shows that POME is suitable to be solid fuel because of high calorific value because it reached the average value to become solid fuel which was 16MJ/kg. Therefore, solid POME is very suitable to act as solid fuel.

B. TGA Analysis

The TGA and DTG curves for the POME solid powder are presented in Figure 1. The TGA curve shows that the weight loss percentage increase with the increase of temperature. The DTG curve shows the same tendency. The small peak, which occurs around 100℃, is owing to release moisture. The second-high peak which takes place around 350℃ is due to the breakdown of the macromolecular structure of solid POME and the release of volatile products. The parameters ignition temperature (Tign), maximum temperature (Tmax), transition temperature (Tg) were deduced from the TGA curves. The overall sample weight loss per unit time was 3.05 $\%min^{-1}$. From Figure 1, it can be deduced that POME solid powder decomposition occurs in four (4) stages; drying (A), heating (B), devolatilization (C) and char aggregation (D).

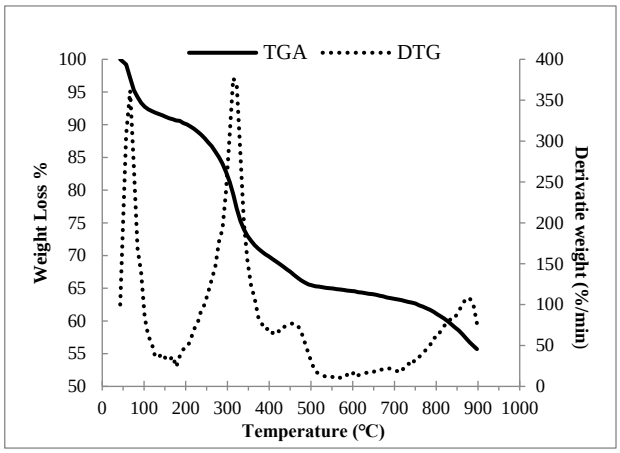

Figure 1: TGA and DTG curve of POME solid powder

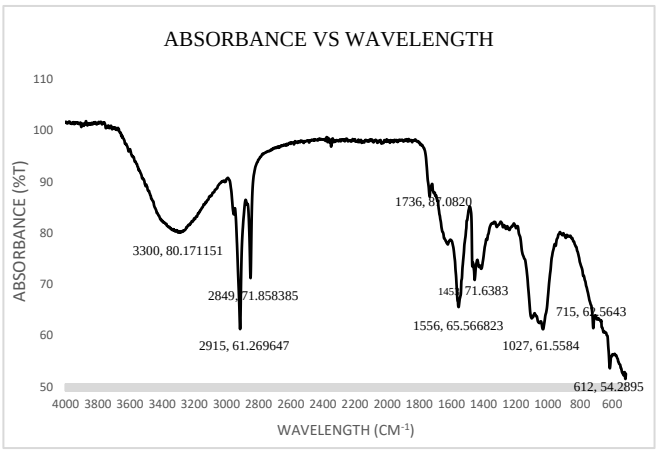

Figure 2: IR spectra of solid POME

The fuel ignition temperature (Tign) signifying the onset of devolatilization was 300°C. The peak temperature of devolatilization was 400°C and is denoted as glass transition (Tg) or maximum temperature (Tmax) as deduced from the TGA and DTG graph.

In addition, two peaks were observed in the DTG curve of the sample. The first peak between observed from 58°C to 100°C denoting the drying process of the reaction. Sample weight loss during this stage was 5%. The second peak between 206°C and 400°C signifies the devolatilization of the sample. During this stage of the reaction, the condensable and non-condensable matter in the fuel is thermally decomposed into gases, char, and tar. Sample weight loss during this step of the reaction is 80% of the initial sample weight. The TGA and DTG temperature and weight loss profile of the sample is presented in Table 3.

Table 4: Proximate analysis of POME solid powder (wt., %)

Stage	Process	Onset (°C)	End (°C)	wt % Loss	Time (mins)
A	Drying	58	100	5.0	3.90
B	Heating	150	200	5.06	7.80
C	Devolatization	206	400	40.55	23.40
D	Char aggregation	600	900	45.71	42.47

The results in **Table 4** indicate that the thermal decomposition of the solid powder from 50°C to 900°C resulted in approximately 80% of the sample. Hence, higher heating rates and temperatures greater than 900°C are required to ensure complete decomposition of the solid fuel into the desired products of thermal conversion.

C. Fourier Transform Infra-Red spectroscopic (FTIR)

The results in Table 5 shows the functional group in the solid POME after dried in the oven for 30minutes. FTIR spectroscopy was used to differentiate the functional group in the solid POME. Determination of the functional group of the sample reflected by the variation in their FTIR spectra patterns based on the range shown in Table 1.

Table 5: Major absorption in infrared spectra of solid POME.

Peak No.	Wavelength (cm^{-1})	Definition of the spectra
1	3300	Water OH stretch
2	2915	-C-H stretch
3	2849	-C-H stretch
4	1736	C=O ester
5	1556	C=C aromatic
6	1453	CH_2 bend
7	1027	C-OH stretch
8	715	C-Br
9	612	C-Br

The sample was analyzed using FTIR spectroscopy exhibit characteristics absorbance patterns at a wavelength between 4000 and 400 cm^{-1}. Table 5 shows all the major functional group exists in the infrared spectra of the solid POME. The result shows a strong bond around 3300 cm^{-1} is strongly suggested as OH group were usually known as water OH stretch group occurs in the hydrogen bond which the spectrum of alcohol.

The others IR spectra for the region where the range between 2840 and 2950cm^{-1} shows the functional group of alkyl-C-H stretch which is the spectrum of hexanoic acid and also for 1027$cm^{-1}$with functional group of C-OH stretch, for 1736cm^{-1} shows the functional group of C=O ester can be categories as the spectrum of butyraldehyde. Then, for the region at 1556cm^{-1}, 1453cm^{-1} are C=C aromatic usually known as alkenes group and CH_2 bend known as alkyl halides compound respectively. Lastly, for the IR region lower than 1000cm^{-1}, where it can be classified as alkyl halides are compounds that have a C–X bond, where X is a halogen either bromine, chlorine, fluorine, or iodine. Therefore, from the result, solid POME can be classified as environmentally friendly to be used as solid fuel.

IV. CONCLUSION

The solid fuel properties of POME solid were analyzed in this study. The results showed that the fuel contains low moisture content at 8.17%, low ash content at 4.56%, high fixed carbon at 15.44%, high volatile matter content at 71.83%. In addition, nitrogen and sulfur were present in trace quantities indicating thermal conversion of the fuel will result in very low concentrations of SO and NO. From the combustion process, it shows that solid POME is suitable for being the initiator for the combustion process with calorific value at 15.9MJ/kg. The TGA results showed that the thermal decomposition of the fuel occurs in four stages with devolatilization commencing at 206°C. The devolatilization process peaks at 400°C and denoted as Tmax resulting in a 45% weight loss of the sample. As a result, from FTIR with a range of wavelength between 4000cm^{-1} to 500cm^{-1}, it was observed that the majority functional group in solid POME were alcohol, hexanoic acids, butyraldehyde, alkenes group, and alkyl halides. The results show that POME solid fuel is an environmentally friendly fuel.

ACKNOWLEDGMENT

Thank you to Mr. Sharizan Najib, Mr. Mohibah Musa, Mdm, Roswati Hasim, Mdm Rohaida Zainordin, Universiti Teknologi MARA and Sime Darby Plantation Berhad for supporting and guidance in completing this research project.

V. REFERENCES

[1] T. Cheng Hai, "The palm oil industry in Malaysia: From seed to frying pan," *WWF Malaysia*, no. November, p. 145, 2002.

[2] M. A. Sukiran, F. Abnisa, W. M. A. Wan Daud, N. Abu Bakar, and S. K. Loh, "A review of torrefaction of oil palm solid wastes for biofuel production," *Energy Convers. Manag.*, vol. 149, pp. 101–120, 2017.

[3] T. H. Oh, M. Hasanuzzaman, J. Selvaraj, S. C. Teo, and S. C. Chua, "Energy policy and alternative energy in Malaysia: Issues and challenges for sustainable growth – An update," *Renew. Sustain. Energy Rev.*, vol. 81, no. July 2017, pp. 3021–3031, 2018.

[4] S. Mekhilef, A. Safari, W. E. S. Mustaffa, R. Saidur, R. Omar, and M. A. A. Younis, "Solar energy in Malaysia: Current state and prospects," *Renew. Sustain. Energy Rev.*, vol. 16, no. 1, pp. 386–396, 2012.

[5] N. Aghamohammadi, S. S. Reginald, A. Shamiri, A. A. Zinatizadeh, L. P. Wong, and N. M. B. N. Sulaiman, "An investigation of sustainable power generation from oil palm biomass: A case study in Sarawak," *Sustain.*, vol. 8, no. 5, pp. 1–19, 2016.

[6] N. Dewayanto, M. Haizal, M. Husin, and M. R. Nordin, "Jurnal Teknologi SOLID FUELS FROM DECANTER CAKE AND OTHER," no. October 2015.

[7] Y. Shiratori, T. Q. Tran, Y. Takahashi, and K. Sasaki, "Application of Biofuels to Solid Oxide Fuel Cell," vol. 35, no. 1, pp. 2641–2651, 2011.

[8] W. P. Q. Ng, H. L. Lam, F. Y. Ng, M. Kamal, and J. H. E. Lim, "Waste-to-wealth: Green potential from palm biomass in Malaysia," *J. Clean. Prod.*, vol. 34, no. September 2011, pp. 57–65, 2012.

[9] S. Yusoff, "Renewable energy from palm oil - Innovation on effective utilization of waste," *J. Clean. Prod.*, vol. 14, no. 1, pp. 87–93, 2006.

[10] H. C. Ong, T. M. I. Mahlia, and H. H. Masjuki, "A review on energy scenario and sustainable energy in Malaysia," *Renew. Sustain. Energy Rev.*, vol. 15, no. 1, pp. 639–647, 2011.

[11] S. M. Yahaya and S. Lau, "Palm oil mill effluent (POME) from Malaysia palm oil mills: Waste or resource," *Int. J. Sci. Environ. Technol.*, vol. 2, no. 6, pp. 1138–1155, 2013.

[12] K. Fujine, "FlashEA 1112 Elemental Analyzer (CHNS): User Guide," *Int. Ocean Discov. Progr.*, no. January, pp. 1–12, 2014.

[13] Y. Y. Chong, S. Thangalazhy-Gopakumar, S. Gan, H. K. Ng, L. Y. Lee, and S. Adhikari, "Kinetics and Mechanisms for Copyrolysis of Palm Empty Fruit Bunch Fiber (EFBF) with Palm Oil Mill Effluent (POME) Sludge," *Energy and Fuels*, vol. 31, no. 8, pp. 8217–8227, 2017.

[14] P.December, "Biological_Treatment_of_Palm_Oil_Mill_Effluent_(Pome)_Using_an_Up-Flow_Anaerobic_Sludge," no. December 2006.

[15] A. Bryś *et al.*, "Wood biomass characterization by DSC or FT-IR spectroscopy," *J. Therm. Anal. Calorim.*, vol. 126, no. 1, pp. 27–35, 2016.

[16] "Calorific Value or Heating Value of the Fuel & Moisture Content: Burning Coal in Power Plants." [Online]. Available: https://www.brighthubengineering.com/power-plants/22202-burning-coal-in-power-plants-calorific-value-and-moisture/. [Accessed: 23-May-2019].

[17] B. B. Nyakuma, A. Johari, A. Ahmad, and T. A. T. Abdullah, "Thermogravimetric analysis of the fuel properties of empty fruit bunch briquettes," *J. Teknol. (Sciences Eng.*, vol. 67, no. 3, pp. 79–82, 2014.